Comment on "Theory of vibrational overtone line shapes of polyatomic molecules"

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Importance of the local mode concepts for understanding X–H (X = C, N, O) stretching overtone spectra in polyatomic molecules is now being recognized.[1] In particular, peak positions of overtones are easily assigned with energy levels of a local Morse potential system. As to line shapes of overtones, recently, Heller and Mukamel[2] have proposed a theory based on the local mode interactions, keeping the experiments by Bray and Berry on the overtone spectra of benzene in mind. In this theory all other normal modes except for the four C–H stretching normal modes are regarded as a "heat bath" perturbing the six equivalent local C–H modes. Their final expression for widths of overtones is given by [see Eq. (25b) in Ref. 2]

$$\tilde{\Gamma}_s \approx \frac{D_m \mid V_{sm} \mid^2 \Gamma_m}{(\epsilon + \Delta E_{sm})^2 + \frac{1}{2}\Gamma_m)^2} \ .$$

They could almost simulate the Bray and Berry's results assuming $\mid V_{sm} \mid = 50\sqrt{s}$ cm^{-1} and $\Gamma_m = 500$ cm^{-1}. Here V_{sm} denotes the interactions between the sth state of the local mode prepared by a photon and the accepting other local mode ground states, and Γ_m, the decay constant of the accepting local mode state due to interactions with the heat bath. Although this theory is very simple and is in very good agreement with the experiments, it appears that the values ($\Gamma_m = 500$ cm^{-1} and $\mid V \mid_{sm} = 50\sqrt{s}$ cm^{-1}) they assumed are too large. As can be seen from the fact that the four C–H normal mode frequencies are 3056 ~ 3073 cm^{-1}, the local mode interactions may not exceed $10\sqrt{s}$ cm^{-1} even in low-lying states. For higher excited states, the local mode representation becomes much more preferable.[1] Thus, other theories with realistic parameter values may be necessary.

Our conclusion is that, in the Heller and Mukamel's theory, only the local mode interactions V^{LL} should be replaced by the local mode–normal mode interactions $V^{LM} = \sum_{ijk} d_{ijk} R_i Q_j Q_k$. In this case many combination bands can couple to the prepared local mode (R_i). Among them we choose some effective accepting combination modes under the conditions:

(1) They must contain at least one of the a_{1g} ring breathing (ν_1), e_{1u} C–C stretching (ν_{19}), b_{1u} C–C–C bending (ν_{12}), and e_{2g} C–C–C bending (ν_6).

(2) Their frequencies are 2300~2650 cm^{-1}. The reason why those modes in condition (1) are particularly important is as follows: first of all, note that C_i and H_i motions on the C_i–H_i line in benzene are separated to their relative (i.e., stretching) motion and that of the center of gravity. As long as the C_i–H_i stretching motion is harmonic the two motions decouple each other, even though the C_i–H_i stretching mode is highly excited. However, if the excited oscillator is an anharmonic one, both the motions will strongly couple. Thus, we intuitively understand that the above mentioned four normal modes to which the motion of center of gravity contributes effectively interact with the highly excited local C_i–H_i stretching mode. Condition (2) is added, because we are now keeping the fifth through seventh C–H overtone spectra of benzene in Bray and Berry experiments in mind. Thus, as the accepting modes, we now have 11 combination bands ($\nu_1+\nu_3$, $\nu_1+\nu_8$, $\nu_1+\nu_{14}$, $\nu_1+\nu_{19}$, $\nu_{12}+\nu_3$, $\nu_{12}+\nu_8$, $\nu_{12}+\nu_{14}$, $\nu_{12}+\nu_{19}$, $\nu_{19}+\nu_9$, $\nu_{19}+\nu_{15}$, $\nu_{19}+\nu_{18}$).[4] In this model we can obtain $\tilde{\Gamma}_s \sim 100$ cm^{-1} assuming $\Gamma_m \sim 50$ cm^{-1} and $\mid V \mid_{sm} \sim 10\sqrt{s}$ cm^{-1}. For example, taking $\Gamma_m = 50$ cm^{-1} and $\mid V \mid_{sm} = 12\sqrt{s}$ cm^{-1} for the fifth overtone ($s = 5$), we have $\tilde{\Gamma}_5 = 114$ cm^{-1}. A further refinement of those values ($\tilde{\Gamma}_s$) may be meaningless since our model contains too many unknown parameters. We think, however, that, although our model is not as simple as that of Heller and Mukamel, the parameter values assumed here may be much more realistic.

Figure 1(a) schematically represents the photo-absorption process of the C–H local mode. While the hole state (0) is almost unperturbed, the particle state ($\tilde{s}$) should be renormalized because of the interactions with the accepting normal modes, as discussed above, which are also perturbed by the heat bath. Hence, the particle propagator is a solution of the Dyson equation shown in Fig. 1(b). The second-order diagram of the self-energy is given in Fig. 1(c). The interaction denoted by the broken lines is now V^{LM}. The matrix element in this

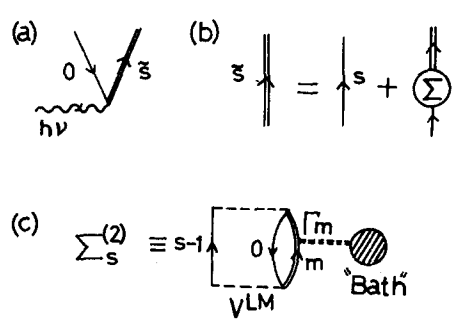

FIG. 1. (a) Diagrammatical representation of the local mode excitation process. (b) Dyson equation satisfied by the particle propagator. (c) Diagrammatic expression of the second-order self-energy in the heat bath.

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diagram is given by $V_{sm} = \langle s-1 | \langle m | \sum_{ijk} d_{ijk} R_i Q_j Q_k | 0 \rangle | s \rangle$, explicitly. Here, if $j = k$, $|m\rangle$ is the second excited state of the accepting normal mode j and also, if $j \neq k$, $|m\rangle$ stands for the combination state $|1\rangle |1\rangle$ of the accepting normal modes j and k. The imaginary part of $\sum_s^{(2)}$ gives the width of the sth overtone. In addition, if V^{LL} is used instead of V^{LM} in this diagram, it is of course the Heller and Mukamel's model.

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[3]R. G. Bray and M. J. Berry, J. Chem. Phys. 71, 4909 (1979).
[4]Here we have used the Lord's notation.